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Enhancement of the transport and dielectric behaviour of pure and blended CPVC by metal ions

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Abstract : The AC conductivity and the dielectric properties were measured as a function of temperature and frequency for the pure and blended chlorinated polyvinyl chloride (CPVC) polymer samples. The DC conductivity was measured in the same range of temperature. The effect of metal ion concentration as well as its ionic radius on the above properties was studied. The measurements of conductivity showed the existence of more than one conduction mechanism. Both DC and AC conductivities increase with increasing the metal ion content. The obtained values of the activation energy indicate the semi conducting behaviour for metal-doped samples.

Keywords : Polymer, AC and DC conductivity, dielectric property.

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The electrical properties of chlorinated polyvinyl chloride (CPVC) are of great interest because of their wide range of applications, which can be considered as one of the easily molded insulation. These properties depend not only on their chemical composition and structural features but also on the degree of molecular order. The polymer conductivity depends on the presence of free ions, which are not connected chemically with the polymer chain while the main chain may not participate in the charge transfer process. Thus, the polymer conductivity depends greatly on the presence of low molecular weight impurities, which can serve as an ion source [1]. In polymers, there are two possible ion sources, the former is the dipole orientation by thermal agitation and the latter is the ions, which are injected from the metal electrode into the polymer system [2,3]. The chlorinated polyvinyl chloride (CPVC) is known to undergo thermal and chemical dehydrochlorination [4,5]. Thermal degradation is believed to proceed almost exclusively by dehydrochlorination resulting in polyene sequences when the temperature is raised at a constant rate. The investigation of dielectric properties of polymeric materials is one of the most convenient methods of unraveling the origin of dielectric dispersion and relevant phenomena [6–8]. The AC conductivity measurements are very important to characterize the nature of the conduction process. Studies of polymers provide valuable information about molecular motion and their interaction in the composite materials. The aim of the present work is to find a good correlation between the metal ion concentration as a dopant material and the electrical properties of the CPVC and also to find the effect of the ionic radii of different dopants used on such properties.

The samples under investigation are prepared using the standard casting method in which the pure CPVC is dissolved in dry tetra hydroflurine (THF) [British Drug House (BDH)]. The inorganic compounds (metal acetates) are also dissolved in (THF) and then blended with CPVC in proper weights (1, 2, 3 and 4 wt%). The resulting mixture is casted in a level petridish of diameter 10 cm and left to dry in a level dissicator for 3 days. The obtained uniform thickness thin films are checked for good drying and then cut in the form of disks with diameter 10 mm and thickness 0.05 mm. Differential

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scanning calorimetry (DSC) thermographs are performed for all prepared samples in the same range of temperature including the glass transition temperature. For measuring the electrical properties, two surfaces of each film are coated with silver paint and checked for good conduction. The two-probe method has been used for measuring all electrical properties, where Hioki LCR-Z Hi tester (Japan) model 3531 is used for such measurements. DC conductivity of all samples are measured at a fixed voltage of 600 V, not exceeding 1.2×10^5 V/cm. The temperature of the sample is measured using T-type thermocouple with its junction just in contact with the sample where the accuracy was ±1°C.

DC electrical conductivity :

The dependence of σ_{DC} on the reciprocal of the absolute temperature for CPVC, pure and Cu-doped sample is shown in Figure 1. The results show that the conductivity for all samples is increased with increasing both temperature and the metal ion concentration. It must also be noted that the conductivity of the doped samples is always more than that of the pure one. The increase in σ_{DC} at high temperature is due to liberation of more electrons or/and ions through the amorphous region where the thermal energy is sufficiently large. With heating, a microstrain is expected to takes place in the sample, which affects directly on the motion of charge carriers as well as their conductivity [9,10]. This is because the microstrain initiates small polarons move and participate

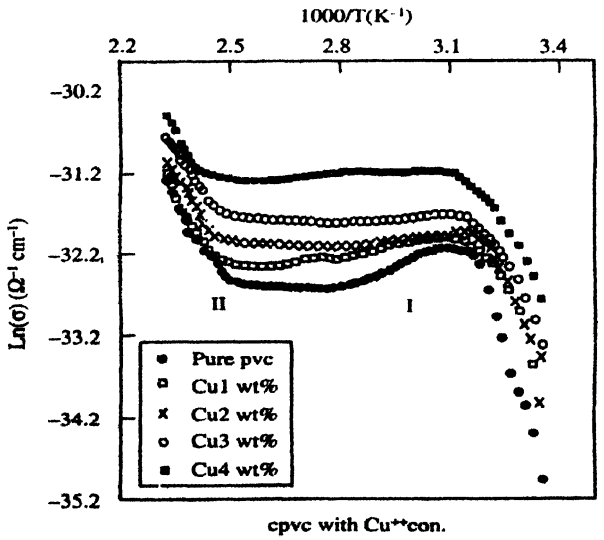

Figure 1. Representation of the DC conductivity (ln σ_{dc}) *vs.* 1000/*T* of pure CPVC and their blends with different concentration (1, 2, 3 and 4 wt%) of [Cu^{2+}].

in conductivity. Two breaks in the figure are observed for all investigated samples. The lower temperature break corresponds to the glass transition temperature (T_g), while the other is related to the crystalline region [11]. The obtained data showed that the DC conductivity increases with decreasing ionic radius of the metal ion where $r_{Cu} < r_{Ni} < r_{Fe} < r_{Cr}$. Also σ_{DC} increases with increasing the metal ion concentration. This result is due to the diffusion of the dopant material into the polymer matrix. At higher temperature (above T_g), the increase in the free volume would facilitate the motion of the ionic charge carriers. Evidently, all the plots of ln σ *versus* 1/*T* indicate the maintenance of the two segments obeying the normal Arrhenius equation $\sigma = \sigma_0 \exp(-\Delta E/kT)$ where σ_0 is the preexponential factor, ΔE is the thermal activation energy and k is the Boltzman constant. The values of the activation energy were calculated from the slopes of ln σ *versus* 1/T for low (E_I) and high (E_{II}) temperature regions respectively and are reported in Table 1. The reported

Table 1. Activation energies E(eV) calculated for CPVC doped with different metal ion concentration in regions I and II.

Sample	Region I	Region II
Pure Cpvc	1.20	0.80
Cu1 wt%	0.81	0.72
Cu2 wt%	0.71	0.61
Cu3 wt%	0.69	0.58
Cu4 wt%	0.64	0.53
Ni1 wt%	0.85	0.73
Ni2 wt%	0.79	0.55
Ni3 wt%	0.72	0.58
Ni4 wt%	0.67	0.56
Fe1 wt%	0.87	0.75
Fe2 wt%	0.82	0.68
Fe3 wt%	0.74	0.60
Fe4 wt%	0.68	0.58
Cr1 wt%	0.89	0.79
Cr2 wt%	0.85	0.70
Cr3 wt%	0.77	0.63
Cr4 wt%	0.70	0.60

data show that the activation energies are decreased with increasing metal ion concentration. In general, the values of the activation energy more than 0.6 eV would normally be associated with ionic transport [3]. The value of activation energy less than 0.2 eV should be associated with electronic mechanism. Therefore, it is acceptable to suggest here that at the two regions I and II, the conduction may be due to ionic mechanism and space charge limited current. The CPVC doped with Cu^{2+} ion

has the lowest value of activation energy in comparison with other samples. In fact, transition metals such as Cu^{2+}, Ni^{2+}, Fe^{2+} and Cr^{2+} reside at various sites when introduced in CPVC. They may go substitutionaly into the polymer chain or reside at the amorphous –crystalline boundaries and diffuse preferentially through the amorphous regions and/or charge transfer complexes (CTC) or they may exist in the form of molecular aggregates [12,13]. Thus, it is quite likely that ions of these metals may diffuse in the amorphous phase of the polymer and thus forming (CTC) with polymer chain [14]. Consequently, the maximum conductivity in CPVC samples is obtained when they are doped with Cu^{2+} ions.

AC conductivity :

Figure 2 is a typical curve illustrating the dependence of AC conductivity on the reciprocal of absolute temperature for Cr doped CPVC (concentration of Cr 1 wt%) at different frequencies (10 kHz–1 MHz). From Figure 2, it is clear that nearly same trend was obtained with a large plateau extended over a wide range of temperature. The values of the activation energy in the low temperature region increase with decreasing frequency. This means that in this frequency region, the frequency acts as a pumping force [15] and helps in transferring the charge carriers specially electrons between the different conduction states. At high temperature and high frequency (600 kHz–1 MHz), no detectable increase in the mobility of the charge carriers because the recovering effect of thermal energy increases. The experimental data of the investigated samples showed that σ_{AC} increases with equency. The real cause of increasing σ_{AC} for Cu^{2+} than ıe other metal ions is due to its small ionic radius as eviously discussed in σ_{DC}. The pumping force of the plied frequency helps in pushing the metal ions of maller radius to be moved between the different conduction states with the result of increasing σ_{AC}. This means that the increase of conductivity in CPVC sample for all metal ions is mainly due to thermally activated mobility of ions as the majority of charge carriers and not due to thermally activated creation of charge carriers. The mobility in case of Cu^{2+} ions is much greater than any other metal ions used. The dependence of σ_{AC} on the applied frequency at temperatures 416, 357 and 312 K is shown in Figure 3. It is known that AC conductivity can be represented over many decades of frequency by an empirical relation of the form [16] :

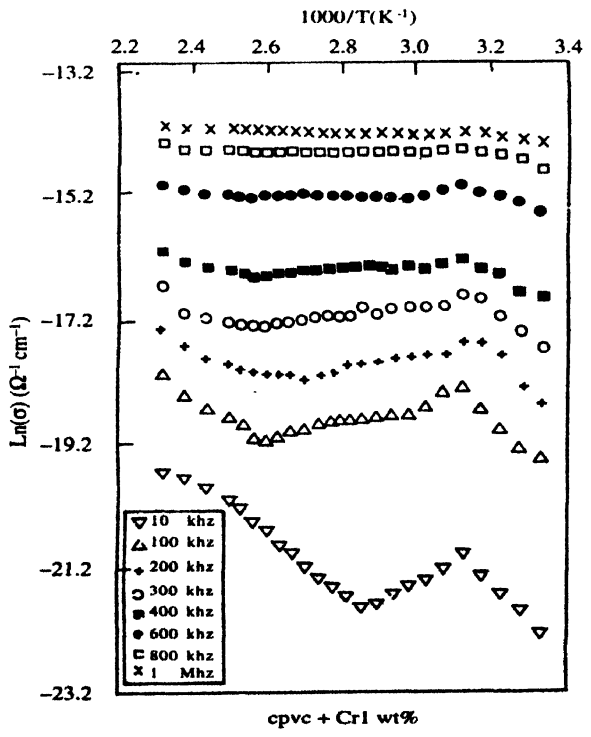

Figure 2. Representation of the AC conductivity at different frequencies (ln σ_{ac}) *vs.* 1000/*T* of CPVC doped with (Cr^{2+}) at concentration 1 wt%.

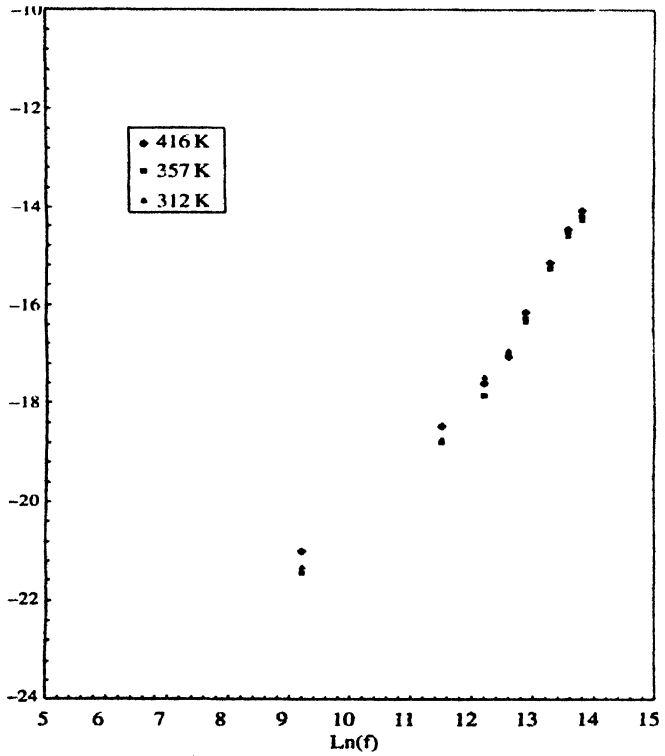

Figure 3. Variation of ln σ_{ac} with ln frequency.

$$\sigma_{AC} = A\omega^s \quad (1)$$

where A is constant and the index s is the exponent of frequency. The calculated values of s are found 1.53, 1.58 and 1.55 at 416, 357 and 312 K respectively. The values for s are significantly higher than unity and independent on temperature. Accordingly, the data gave the prediction that the quantum mechanical tunneling model is the most suitable mechanism to explain the AC conduction behaviour in the considered system [17]. From the comparison between σ_{AC} and σ_{DC}, it could be concluded that the higher conductivity and lower activation energy of AC measurements than those of DC, enhances the dependence of AC conductivity on frequency. Consequently, it can be suggested that the free radicals (carriers) which appear only within CPVC macromolecules, can be more detected in AC than DC measurements. These carriers are retarded by the established barriers between polymer molecules. Thus, the frequency of the applied electric field facilitates the AC conductivity in the sample by means of the Maxwell-Wagner two-layer condenser model [18].

Dielectric constant :

The variation of the activation energy between large values in DC measurement and small values in DC measurement means that both electrons and ions participate in conduction mechanism. The small positive polaron role cannot be neglected in the conduction process. Figure 4 shows the temperature dependence of the real part of the dielectric constant (ε') for pure CPVC at various frequencies in the temperature range (300–430 K). From the figure, it is clear that as the frequency increases, the dielectric constant decreases. This decrease is attributed to the fact that the dipoles of the main chain of CPVC cannot follow up the field variation [19]. The gradual increase of ε' with temperature for all frequencies and the sharp increase above 326 K indicate the glass transition temperature (T_g) of the samples. The increase of ε' with temperature is mainly due to the increase of the polarization arising from the molecular motion of polymer chain segments which in turn, allows the orientation of dipolar units in the applied electric field. But at the same time, the contribution of interfacial polarization gives rise to the space charge mechanism [20]. Figure 5 shows the variation of (ε') with temperature for pure CPVC and doped with metal (Cu^{2+}) concentrations (1, 2, 3 and 4 wt%) at a frequency of 100 kHz. From this figure, it is noted that (ε') increases with increasing Cu content. Such a behaviour was expected because more conducting centers are available in the dielectric medium which absorb the electric energy passing through the medium resulting into the damping of the dipolar motion of the dielectric medium and hence increases the value of (ε') for the samples [21].

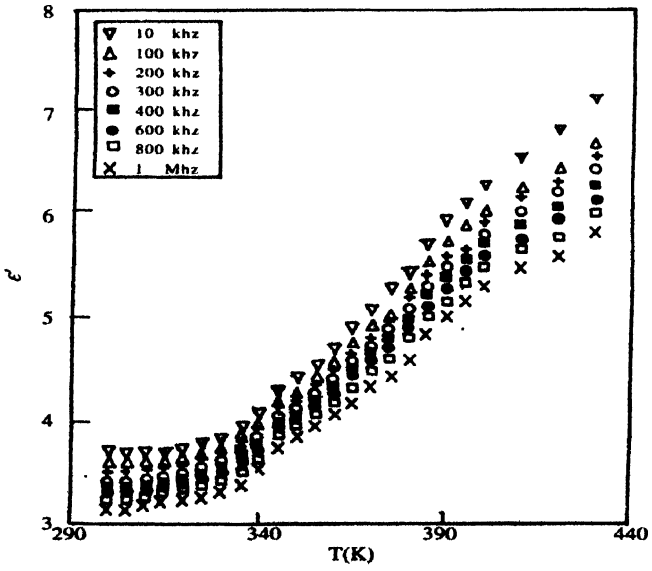

Figure 4. The variation of the dielectric constant ε' with temeperature at frequencies (10 kHz –1 MHz) for pure CPCV.

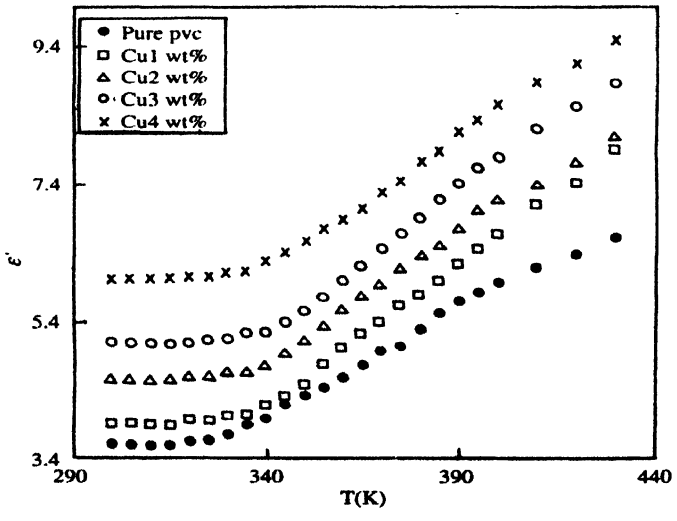

Figure 5. The variation of dielectric constant ε' with temperature for pure CPVC and doped with metal (Cu^{2+}) concentrations (1, 2, 3 and 4 wt%) at (100 kHz).

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